The Influence of Maltodextrins on the Structure and Properties of Compression-Molded Starch Plastic Sheets

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ABSTRACT: Starch plastic sheets were prepared by compression molding of starch-based plastic granulates. The granulates were prepared by extrusion processing of mixtures of granular potato starch and several maltodextrins (5% w/w) in the presence of glycerol and water as plasticizers and lecithin as melt flow accelerator. The materials were semicrystalline, containing B-type, V_h-type, and E_h-type crystallinity. The properties were dependent on water content. For the materials, a brittle-to-ductile transition occurred at a water content in the range of 11–12%, which was in accordance with the observed glass transition temperature. The structural and mechanical properties were a function of starch composition and maltodextrin source as well as molding temperature. The amount of granular remnants and residual B-type crystallinity decreased with increasing processing temperature. The amount of recrystallized single-helical amylose increased with increasing temperature. At molding temperatures in the range of 180–200°C, a sharp decrease in starch molecular mass occurred. The influence of molding temperature was reflected in a sharp increase in elongation at molding temperature above 160°C and a gradual decrease in elastic modulus. The tensile strength showed an initial small increase up to 160°C and a sharp decrease at higher molding temperatures. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2207–2219, 1999

Key words: starch; plasticizer; extrusion; molding; bioplastic; molecular mass

INTRODUCTION

Over the past decades, several starch-based plastic materials have been developed on the basis of nonchemically modified starches and natural or degradable additives such as water, glycerol, and lecithin.[1–4] The starch source is an important factor in the regulation of the properties of starch-based plastics. The native or naturally occurring granular starches differ mainly in amylose and amylopectin content as well as molecular mass, molecular mass distribution, and degree of branching of both types of molecules.[5–7] During thermomechanical processing of starch plastics, such as extrusion and injection molding, starch molecular mass lowered because of the high temperature and shear.[8–12] Furthermore, some starch-based plastics contain significant amounts of several enzymatically treated starches, usually referred to as maltodextrins. These starches consist of a complex mixture of low molecular starch, malto-oligosaccharides, and even glucose. The effects of the presence of maltodextrins on the processing, structure, and properties of starch-based plastics are still unclear. The purpose of this article is to obtain knowledge about the influence of differences in molecular mass distribution and the presence of malto-oligosaccharides on the structure and property of fully biodegradable compression-molded starch-based plastic sheets.

Several investigators have presented a variety of studies dealing with the relations between processing, structure, and properties of starch-based plastics.[9–21] Direct relations are still not clear, partly because of the complex nature of starch plastic materials. Especially in the case of starch blends, the role of starch structure is more difficult to discriminate.[22–26] Therefore, several studies were focused on materials which contained solely starches and additives, such as plasticizers and melt flow accelerators, thermomechanically processed at relatively low water contents (less than 30% w/w). In particular, the influence of the starch source on the structure and properties of materials in the rubbery state has been studied.[9–12,19–21] Especially the amylose-amylopectin ratio of the various sources is an important factor.[11] An increase in the amylose content of starch plastic sheets resulted in stronger and stiffer materials with lower elongation. Furthermore, it has been shown that starch molecular mass has a significant effect on the mechanical properties of starch plastics.[12,21] It seemed that rubbery materials composed of low molecular mass starches prepared by acid hydrolysis have lower elongations at break compared with native starch. Until recently, most studies on fully starch-based plastic materials were focussed on rubbery materials and not on glassy materials.

As polymer-chemistry concepts were shown to be applicable to starch-based plastics, the rubber-to-glass transition, expressed as the glass transition temperature (T_g) of the materials determine also the properties.[27–29] Various researchers have studied the influence of water, polyols, and oligosaccharides on the T_g of starch materials.[30–33] More recently, the T_gs of maltodextrins as a model food system have been studied.[34] Several studies have shown that maltodextrin or starch-hydrolysis products in general, exhibit an antistaling effect and affect the mechanical properties (firmness) of starch gels and breads.[35,36]

However, in contrast with breads and gels, starch plastics, destructurization or plasticization of the granular starch is performed at relatively high shear and temperatures, with limited amounts of water but in the presence of other plasticizers such as polyols, giving a macroscopically or even microscopically homogeneous material.[37] At low plasticizer contents, granular swelling, granule disintegration,[38–40] and starch chain mobility is limited. Therefore, granular remnants can still be present.[19,20] Starch chain mobility, dependent on water content during processing, is thought to determine the formation of a complex starch network. This network involves amylose and amylopectin starch chain-chain interactions and entanglements as well as various crystal structures.[20,41–44] The role of other processing parameters, such as temperature, shear and pressure, and the effects of other differences in composition of the premix before plasticization, such as starch source and additives, are still not well understood.

In this study, starch-based plastic materials were prepared at relatively low water contents and without the addition of other polymeric materials such as polyesters. A series of maltodextrins (5% w/w) were mixed with granular potato starch and processed by extrusion and subsequently by compression molding of the extruded granulates at various temperatures. The amounts of plasticizers, i.e., water and glycerol, and lecithin, added as a melt flow accelerator, were held constant. The structural and mechanical properties of the plastic sheets were studied below and at approximately the T_g after aging of the materials at various humidities. The starch structure and morphology were assessed using X-ray diffraction, size-exclusion chromatography coupled with laser light scattering, and light microscopy. The differences in stress-strain behavior of the plastic sheets were related to the variations in processing and aging conditions as well as starch structure and morphology.

EXPERIMENTAL

Materials

L-α-lyso-phosphatidylcholine (LPC) from egg yolk (L-4129) was purchased from Sigma (Zwijndrecht, The Netherlands). Glycerol was obtained from Chemproha Chemicals Distributors (Dordrecht, The Netherlands). (NAT 6-2409; density = 1.26 g/mL). Soy lecithin (Topcithin) was obtained from Lucas Meyer (Zaandam, The Netherlands). Starches were obtained from Avebe (Foxhol, The Netherlands). Native potato starch (Farina), PN, contained 17% water (w/w). The other starches were enzymatically modified amorphous potato starches (usually referred to as maltodextrins or low molecular mass starches) and contained 11% water (w/w). Some characteristics of PN and these low molecular mass starches, referred to as maltodextrins (coded as MD2, MD6, MD10, MD20, and MD30), are summarized in Table I.

Table I Characteristics and Properties of the Various Starches or Maltodextrins

Characteristic or Property	Starch Source					
	PN	MD2	MD6	MD10	MD20	MD30
Water (% ± 0.4%)	17	10	9	9	9	9
Amylose (% ± 4%)	27	11	6	0	0	0
Higher saccharides (mg/g ± 5%)	1000	980	950	930	870	800
Maltotriose (mg/g ± 2%)	0	15	35	40	75	110
Maltose (mg/g ± 2%)	0	5	15	25	40	65
Glucose (mg/g ± 2%)	0	0	0	5	15	25
M_z (kg/mol ± 15%)	183,500	3450	1000	940	42	32
M_w (kg/mol ± 5%)	88,500	630	360	170	91	29
M_n (kg/mol ± 20%)	4500	140	61	33	7	1

The amylose content was calculated on the basis of the complex of long chain amylose with LPC as described in the section "Differential Scanning Calorimetry." The amounts of saccharides, maltotriose, maltose, and glucose were taken from the product data sheets as supplied by Avebe. The average molecular masses (z-average, M_z; weight average, M_w; number average, M_n) were determined as described in the section "Molecular Mass Determination."

Extrusion

Premixes were prepared by mixing 12.0 kg starch [total mass on the basis of starch containing 17% water, i.e., 10.0 kg (87.6%) dry starch and 2.0 kg (14.6 %) water], 1.4 kg (10.2 %) glycerol (plasticizer), and 0.3 kg (2.2 %) lecithin (melt flow accelerator) with a Bear Varimixer R40 during 20 min. A series of premixes was prepared with variations in starch composition. The starch consisted of solely PN starch, coded PN1, or mixtures of 95% (w/w) PN1 with 5% of maltodextrin. The materials with the added maltodextrins MD2, MD6, MD10, MD20, and MD30 were denoted as PN2, PN6, PN10, PN20, and PN30, respectively. Extra water was added to the maltodextrins to compensate for the lower water contents (11%). The ratios starch-to-water-to-glycerol-to-lecithin were kept constant. The premixes were equilibrated in closed bags at room temperature for 1 day before extrusion processing.

The starch granulates were prepared by extruding the premixes with an Extruco TSE 76 counter-rotating twin-screw extruder (length = 1515 mm; diameter = 84.2 mm). The screw rotation speed was 30 rpm. The extruder was operated at 10 A. The temperature profile along the extruder barrel was 70, 120, 110, and 80°C (from feed zone to die). The material melt temperature at the die was 110–120°C. The die pressure was 35–45 bar. The extruded strings were granulated with a RIGI granulator (type TPN/s 350/24). The granulates were milled into powders with particle sizes of less than 220 μm. The powdered granulates were stored at room tempera-

ture and ambient relative humidity (RH) of approximately 50–60% for 1 week before compression molding. The water content was 17.6 ± 0.4% (w/w based on total mass).

Compression Molding

The extruded and powdered granulates were applied to a mold with inner dimensions of 100 × 150 × 2 mm (l × w × h). The outer dimensions of the mold were 300 × 350 mm. The samples were covered with an overhead plastic sheet foil at both sides to facilitate mold release. The mold was placed in a hydraulic PHI press (City of Industry, City of Industry, CA). An initial pressure of 4 tons was applied at room temperature. The mold was then heated to 100°C at a rate of 10°C/min. At 100°C, a pressure of 40 tons was applied. Subsequently, the temperature was raised at 10°C/min to finally reach the end temperature between 120 and 200°C. After this the mold was cooled to room temperature at 10°C/min, and the plastic sheets were released from the mold. The water content directly after cooling was approximately 10–13% (w/w).

Storage Conditions (Conditioning)

The compression-molded sheets were cut into tensile bars. The tensile bars were conditioned at various RH between 30 and 90% for 14 days. All samples were stored at room temperature.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) analyses were performed with a Perkin-Elmer DSC-7.

The gelatinization and melting endothermic transitions, T_gs, and amylose contents were obtained as described previously.[12]

Polarized Light Microscopy

The extruded granulates and compression-molded sheets were sliced and viewed at a magnification ×40 with an Axioplan Universal Microscope. Photographs were taken using the MC100 camera accessory.

X-Ray Diffractometry

Wide-angle X-ray diffraction patterns were measured using a Philips powder diffractometer (model PW3710) and crystallinity was calculated and expressed as described previously.[11,12,45]

Molecular Mass Determination

The starch samples were dissolved in $1M$ sodium hydroxide (4 mg/mL). Molecular masses were determined as described previously.[12] Because of the time-dependent partial molecular breakdown of starch in sodium hydroxide, special care was taken in the dissolution method. All samples were sieved (size < 125 μm) and identical amounts of the powders in the aqueous sodium hydroxide were stirred with a magnetic stirrer for exactly 20 h before measurements. The calculated molecular masses should not be interpreted as highly accurate absolute values but as a good indication of changes in molecular masses due to composition and processing.

Moisture Determination

Because of the tendency of the starch plastic sheets to absorb or desorb water, care was taken to measure the water content immediately before testing. The samples were ground under cryogenic conditions. The water content of the powder (1.0 g, size < 125 μm) was determined gravimetrically with an Infrared dryer (Sartorius MA40 at 95°C).

Stress-Strain Analysis

A model 4310 Instron universal testing machine, operated at a crosshead speed of 10 mm/min and 1 kN, was used for tensile measurements. Dumbbell specimens were cut, according to the ISO 1184-1983 (E) standard, from the sheets immediately following compression molding and storage. Four to six replicates of each material were aver-
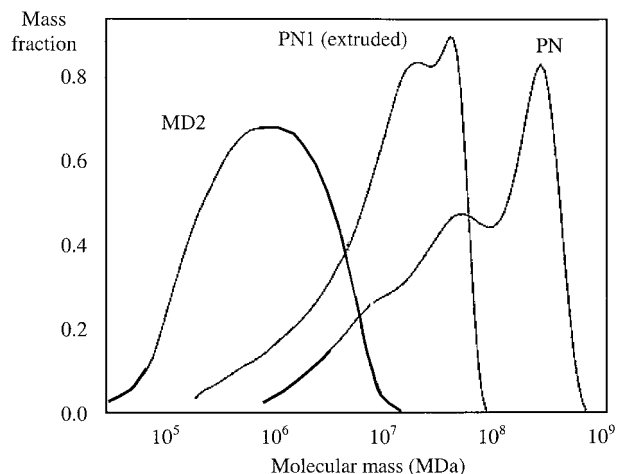
Figure 1 Some typical molecular mass distributions of starch materials as measured with HPSEC-MALLS.

aged. The sheet thickness varied slightly and sample dimensions were corrected individually. The tensile stress at peak or tensile stress (i.e., maximum load) was calculated on the basis of the original cross-sectional area of the test specimen, by the equation: $\sigma = F/A$, where σ was the tensile stress, F was the force, and A was the initial cross-sectional area. The percentage strain or elongation (ε) was calculated on the basis of the length of the narrow parallel portion, by the equation: $(l - l_1)/l_1 \times 100\%$, wherein l was the distance between the gauche marks (in mm) and l_1 was the length of the narrow parallel portion (i.e., 33 mm), which is related to the original gauge length, l_0, by $l_0/l_1 = 25/33$. The elastic modulus (E-modulus) was determined as the initial slope of the stress-strain curve. The measurements were performed at room temperature.

RESULTS AND DISCUSSION

### Structure of the Starch-Based Granulates after Extrusion Processing

Some typical HPSEC-MALLS measurements (shown as molecular mass distributions), of native potato starch, an extruded starch plastic material, and a maltodextrin (MD2), are shown in Figure 1. The weight average molecular mass, M_w, of native potato starch is 88.5 ± 4.5 MDa. The addition of the maltodextrins (5% w/w) reduces the M_w to approximately 84 ± 4 MDa. Because of the large differences between the molecular masses of potato starch and the mal-

todextrins (see Table I), the addition of the maltodextrins does not result in a large change in weight average molecular mass. Because of the addition, a bimodal molecular mass distribution is obtained of a large fraction of a high molecular mass polymer and a small fraction of a low molecular mass polymer with differences in molecular masses and amount of oligomers (maltotriose, maltose, etc.) and monomers (glucose). After extrusion processing the M_w of the material containing solely native potato starch (PN1) but also the materials, which were mixed with the maltodextrins, dropped to approximately 40 ± 5 MDa. The reduction of molecular mass is due to the high shear and high temperature applied during processing.[8–12] The molecular mass determination was not accurate enough to discriminate between the expected differences as a function of maltodextrin source between the various extruded materials.

The amylose content of native potato starch is approximately 27 ± 4%. The amylose content of the MD30 starch, compared with native potato starch, is 0%. Therefore, the amylose contents of the mixtures are only slightly lower. The amylose content of the mixture of 95% PN1 and 5% MD30 (i.e., PN30) is 26 ± 4%. The amylose content after extrusion processing is not significantly reduced. The amylose contents are 25 ± 3 and 23 ± 4 %, respectively, for the material composed of 100% PN1 and PN30. Therefore, it can be concluded that the molecular breakdown during extrusion is for the major part due to the breakdown of the amylopectin fraction.

With polarized light microscopy the extruded materials were studied vs. the type of maltodextrin added. The amounts of intact granules, identified by the typical birefringence of granular potato starch, and granular remnants increased in the extruded starch materials in the series native starch (PN1), PN2, PN6, PN10, PN20, and PN30. The estimated amount (by measuring the area of the granular remnants vs. total area) of granular remnants was between 5 and 10% (w/w).

In Figure 2, the diffractograms are shown of the extruded materials as a function of the type of maltodextrin added. A typical pattern was seen of an almost amorphous, semicrystalline polymeric material. The overall crystallinity was less than 10% (w/w). Two types of crystal structures were identified: the typical amylose single helical structure denoted as V_h-type (19.5°; $2 \times \theta$), and the double helical structure known as B-type (16.8°; $2 \times \theta$).[43] The amount of V_h-type crystals,
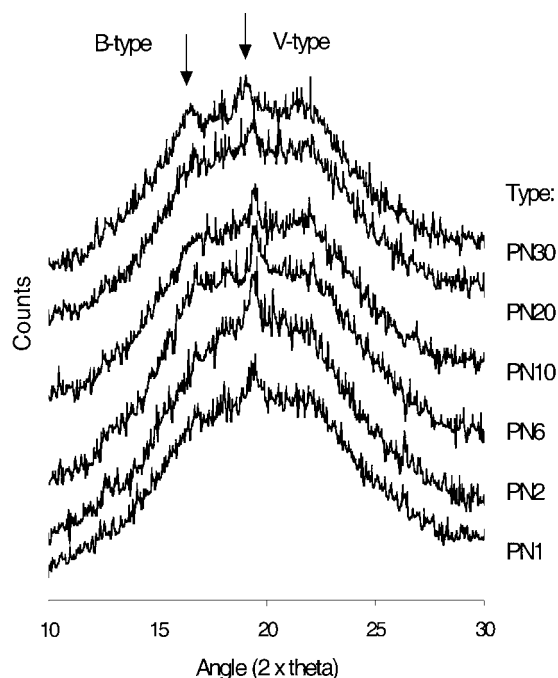
Figure 2 X-ray diffractograms of the extruded starch-plastic materials with different maltodextrins added.

formed after recrystallization of amylose after destructurization or plasticization of the granular starches, decreased linearly {Hc/Ht [at 19.5° (2 $\times \theta$)] from 0.22–0.1} with decreasing molecular mass and increasing amount of oligosaccharides of the maltodextrins added. At the same time the amount of B-type crystallinity increased from 3 to 14% relative to native potato starch.[45] The reduced shear or changed viscosity, due to the increased amount of maltodextrins or oligosaccharides, could explain this observation.[46] As a result, the destructurization of the starch granules would be less as was shown by the presence of more intact granules and granular remnants by light microscopy. No discrimination could be made between residual granular B-type crystals and recrystallized B-type crystals on the basis of powder diffraction. However, most likely the increase in the amount of B-type crystals could be explained by the presence of nonmolten granules and granular remnants, as observed by microscopy, and therewith residual B-type crystallinity which is in accordance with previously reported data.[47,48]

Influence of Molding Temperature and Starch Composition on the Structure of the Starch Sheets

In Tables II and III, the structural differences and the mechanical (stress-strain) properties are

Table II   The Structural and Stress-Strain Properties of Compression-Molded Starch Sheets Composed of Solely (100%) Potato Starch, PN1 (w/w on the Basis of Starch)

T_{melting} (°C)	Structural Parameters			Stress-Strain Properties		
	Crystallinity (Type)[a]	Amylose Content (%)	M_w (MDa)	Stress at Peak (MPa)	E-Modulus (GPa)	Elongation (%)
30–40% RH, 6.5% water, $T_g = \pm 60°C$						
100	V_h	22	35 ± 5	22	1.02	3
120	V_h	24	28 ± 8	25	0.99	4
140	V_h	20	25 ± 4	29	0.99	5
160	V_h	21	27 ± 4	37	0.99	6
180	$(V_h), (E_h)$	19	18 ± 3	36	1.03	6
200	E_h	12	0.5 ± 0.4	16	1.05	3
70–80% RH, 11.1% water, $T_g = \pm 30°C$						
100	(V_h)	22	35 ± 5	12	0.58	4
120	$V_h, (B)$	24	28 ± 8	15	0.64	4
140	V_h	20	25 ± 4	16	0.60	5
160	V_h	21	27 ± 4	17	0.58	6
180	$(V_h), E_h$	19	18 ± 3	17	0.53	7
200	E_h	12	0.5 ± 0.4	5	0.18	27

[a] Crystal type between parentheses means that only a low amount is present.

shown for materials processed at various temperatures and conditioned at 30–40% and 70–80% RH, respectively. Two types of materials were studied, denoted as PN1 and PN30. The structural and stress-strain properties of the influence of starch composition and water content after conditioning are summarized in Table IV.

In Table II the results are tabulated of the PN1 starch plastic materials with a relatively small starch molecular mass distribution (composed of

Table III   The Structural and Stress–Strain Properties of Compression-Molded Starch Sheets Composed of PN30, 95% PN1, and 5% MD30 (w/w on the Basis of Starch)

T_{melting} (°C)	Structural Parameters			Stress-Strain Properties		
	Crystallinity (Type)[a]	Amylose Content (%)	M_w (MDa)	Stress at Peak (MPa)	E-Modulus (GPa)	Elongation (%)
30–40% RH, 6.4% water, $T_g = \pm 60°C$						
100	$V_h, (B)$	21	35 ± 5	20	1.00	4
120	$V_h, (B)$	22	30 ± 7	25	1.00	5
140	V_h	19	35 ± 4	25	0.90	7
160	V_h	19	30 ± 3	27	0.88	7
180	$(V_h), (E_h)$	21	4 ± 3	24	0.98	6
190	E_h	17	1 ± 2	12	0.99	4
70–80% RH, 11.8% water, $T_g = \pm 30°C$						
100	V_h, B	21	35 ± 5	11	0.51	4
120	$V_h, (B)$	22	30 ± 7	12	0.49	5
140	V_h	19	35 ± 4	12	0.42	7
160	V_h	19	30 ± 3	11	0.38	18
180	$(V_h), (E_h)$	21	4 ± 3	8	0.26	63
190	E_h	17	1 ± 2	4	0.10	69

[a] Crystal type between parentheses means that only a low amount is present.

Table IV   The Influence of Molecular Mass on the Structure and Properties of Compression-Molded Starch Plastic Sheet Conditions at Various Humidities

Starch (Code)	Structural Parameters			Thermal and Stress-Strain Properties			
	Crystallinity (Type)[a]	M_w (MDa)	M_n (MDa)	T_g (°C)	Stress at Peak (MPa)	E-Modulus (GPa)	Elongation (%)
35–40% RH, 7.6 ± 0.2% water							
PN1	V_h	27	12	55	33	0.89	9
PN2	V_h	n.d.	n.d.	57	30	0.96	9
PN6	V_h	n.d.	n.d.	51	23	0.92	7
PN10	V_h	n.d.	n.d.	52	18	0.90	7
PN20	V_h	n.d.	n.d.	55	17	0.95	9
PN30	V_h	30	11	54	15	1.07	9
55–65% RH, 9.7 ± 0.2% water							
PN1	V_h	27	12	45	23	0.87	5
PN2	V_h	n.d.	n.d.	40	25	0.87	5
PN6	V_h	n.d.	n.d.	46	21	0.88	4
PN10	V_h	n.d.	n.d.	33	19	0.77	5
PN20	V_h	n.d.	n.d.	37	20	0.87	5
PN30	V_h	30	11	40	19	0.81	5
75–80% RH, 12.2 ± 0.5% water							
PN1	V_h	27	12	28	9.5	0.32	44
PN2	V_h	n.d.	n.d.	30	10	0.35	42
PN6	V_h, (B)	n.d.	n.d.	27	8.7	0.30	33
PN10	V_h, (B)	n.d.	n.d.	24	6.9	0.24	30
PN20	V_h, (B)	n.d.	n.d.	20	6.2	0.19	40
PN30	V_h, (B)	30	11	19	4.7	0.08	79

The various low molecular mass starches or maltodextrins (5% w/w on the basis of starch) were added to obtain differences in molecular mass and molecular mass distribution.

n.d., not determined.

[a] Crystal type between brackets means that only a low amount is present.

solely native potato starch). The materials conditioned at 30–40% RH had a water content (w/w on the basis of dry matter) of 6.5 ± 0.2%. The T_g of these glassy materials was approximately 60 ± 5°C. The materials stored at 70–80% RH had a water content of 11.1 ± 0.3%, which resulted in a T_g of approximately 30 ± 5°C. The DSC thermograms showed very broad glass-to-rubber transitions of more than 20–30°C, which could indicate the presence of a rather heterogeneous polymeric matrix.

In Table III the results are tabulated of the PN30 starch plastic materials with a relatively high amount of low molecular mass starch and saccharides (composed of native potato starch and 5% maltodextrins, MD30). The PN30 containing materials conditioned at 30–40% RH had a water content of 6.4 ± 0.4% (w/w on the basis of dry matter). The T_g of these glassy materials was approximately 60 ± 5°C. The materials stored at

70–80% RH had a water content of 10.8 ± 0.3%, which resulted in a T_g of approximately 30 ± 5°C. Because of the inaccurate DSC data, no significant differences were detected in T_g as a function of starch composition, although for the (rubbery) materials stored at 70–80% RH, there was a slight trend of decreasing T_g with increasing amount of malto-oligosaccharides.

With the aid of polarized light microscopy it was shown that the compression-molded materials showed less birefringence, characteristic of intact native starch granules, than the extruded materials. The amount of intact granules and partially disrupted granular rest structures (remnants) decreased with increasing molding temperature. Above 140°C no birefringence was observed. No significant differences were observed anymore as a function of starch composition, in contrast with the extruded granulates.
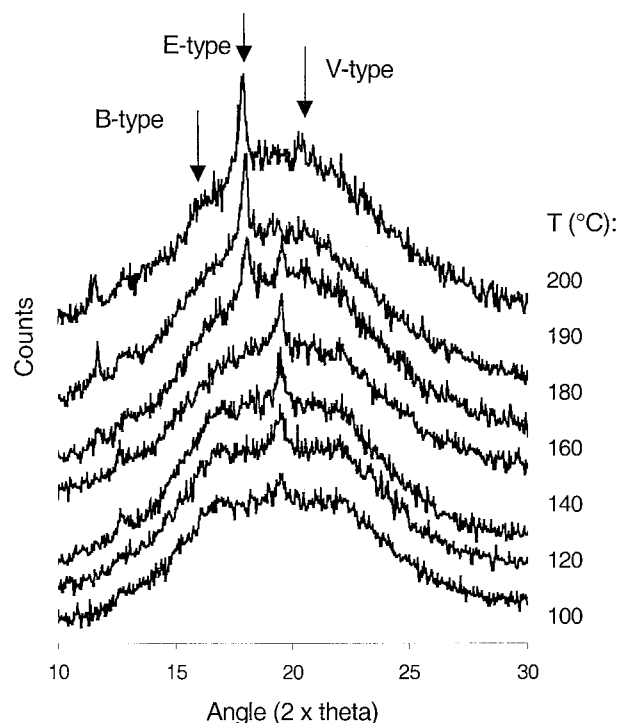
Figure 3 X-ray diffractograms of the molded starch-plastic materials after extrusion and compression molding at different temperatures.

In Figure 3, several typical X-ray diffractograms are shown of the materials compression molded at different temperatures and conditioned for 14 days at 75% RH. The molded materials showed a pattern characteristic of a semicrystalline polymeric material. The materials showed less B-type crystallinity (as indicated by the characteristic peak at a diffraction angle $2 \times \theta$ of 16.8°) after compression molding compared with the extruded materials. Above a molding temperature of 120°C no residual B-type crystallinity was observed. This concurs with the fact that the starch granular structures were completely disintegrated as observed with microscopy. The crystallinity of the materials measured directly after compression molding was compared with the crystallinity of the aged materials. No significant changes were observed due to retrogradation. Retrogradation or recrystallization of especially amylopectin is still limited and unlikely to occur because the materials are above or close to the glass-to-rubber transition.[49]

Single helical-type amylose crystallinity was observed identified as E_h-type and V_h-type.[42,43] The relative amount increased with increasing molding temperature. These structures are due to

recrystallization of amylose after melting of the starch granules. Above 180°C the formation of the E_h-type is preferred over the V_h-type structure. No clear differences in crystallinity were seen between the materials containing 5% of the various maltodextrins and the molded PN1 materials without the presence of malto-oligosaccharides.

From Tables II and III it is shown that molecular breakdown occurred because of the thermomechanical processing at higher temperatures (180–200°C). The materials showed a yellow-brownish discoloration above 180°C. The amylose content is not significantly reduced due to compression molding between 120 and 180°C compared with the amylose content of native potato starch. The amylose content was approximately $22 \pm 2\%$. Above 180°C the amylose content is significantly reduced to 17% at 190°C and 12% at 200°C, respectively. No significant differences were observed between amylose contents as a function of composition (see Table IV). With the aid of HPSEC-MALLS, it was also shown that molecular breakdown of the amylopectin fraction occurred during thermomechanical processing. Although the breakdown was relatively small, between 120 and 160°C, a significant reduction was measured at molding temperatures between 180 and 200°C as is shown in Figure 4. It was not clear if the sharp decrease in molecular mass at high temperatures was related to the formation of E_h-type structures (see Fig. 3). There were no
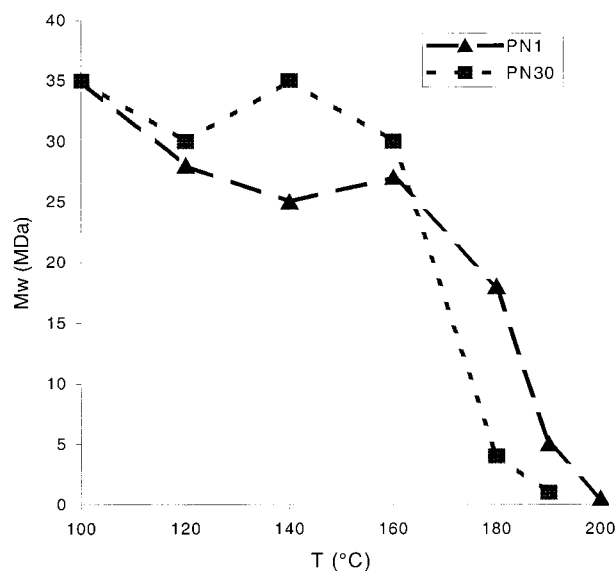
Figure 4 Influence of molding temperature on molecular mass of starch plastics composed of PN1 (▲) and PN30 (■).

significant differences in the number and weight average molecular masses of the various starch sheets with differences in composition molded at 160°C (see Table IV). However, it has to be said that the measured average molecular masses only reflect the differences in the starch polymeric or high molecular mass fraction and not the differences in malto-oligosaccharides. Clearly, the amount of oligosaccharides increased within the series, PN1, PN2, PN6, PN10, PN20, and PN30.

Influence of Molding Temperature on the Stress-Strain Properties of the Sheets

The molded starch materials showed typical stress-strain behavior of starch-based plastics as reported previously.[12,17,19,47] The materials stored at 30–40% RH showed the typical brittle fracture characteristic of a glassy starch material stored below the glass-to-rubber transition. The glassy materials had an elastic modulus of approximately 0.8–1 GPa. No significant differences were observed as a function of processing temperature or starch composition. The tensile stress (or stress at peak) showed a dependence of processing temperature and of starch composition as shown in Figures 5 and 6. The tensile stress and elongation of the potato starch (PN1) materials increased from 22 MPa and 3% (at 120°C) to a maximum of 37 MPa and 6% (at 160°C) and subsequently decreased to 16 MPa and 3% (at 200°C), respectively, for the stress and elongation. A similar profile was seen for the maltodextrin containing molded material. The tensile stress and elongation of the maltodextrin starch materials increased from 20 MPa and 4% (at 120°C) to a maximum of 27 MPa and 7% (at 160°C) and subsequently decreased to 12 MPa and 4% (at 190°C), respectively, for the stress and elongation. A remarkable difference was seen because the tensile stress at the optimum (at 160°C) was significantly lower for the maltodextrin materials. Besides this, the drop in tensile stress was more pronounced for the maltodextrin materials.

Many of the materials stored at approximately the glass-to-rubber transition showed a brittle fracture with elongations in the range of 4 to 7%. The small differences are mainly due to the inaccuracy of the measurements (standard deviations of several percents are observed). For brittle materials, small inhomogeneities due to local differences in processing conditions in the materials could possibly be the reason for the differences in elongation.[48] However, no real structural evidence could be found yet to substantiate this as-
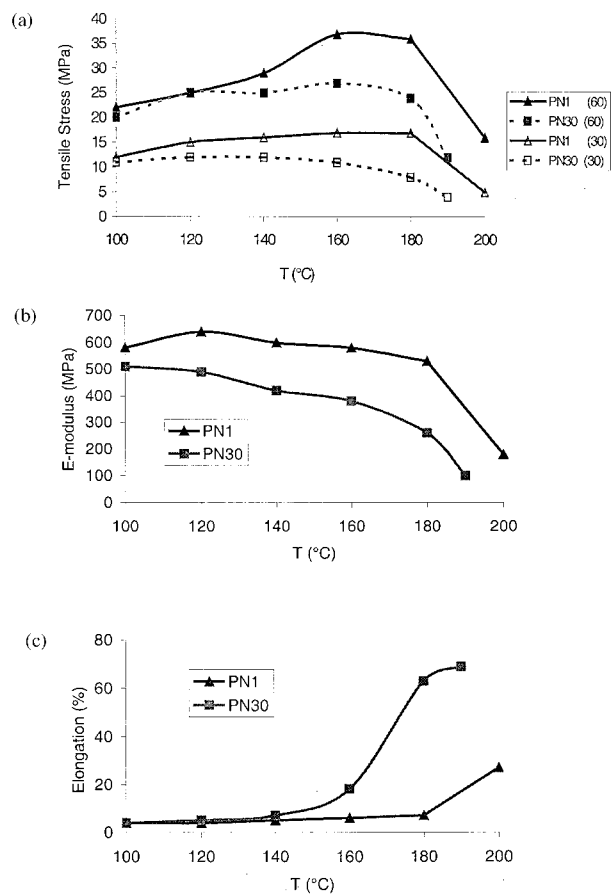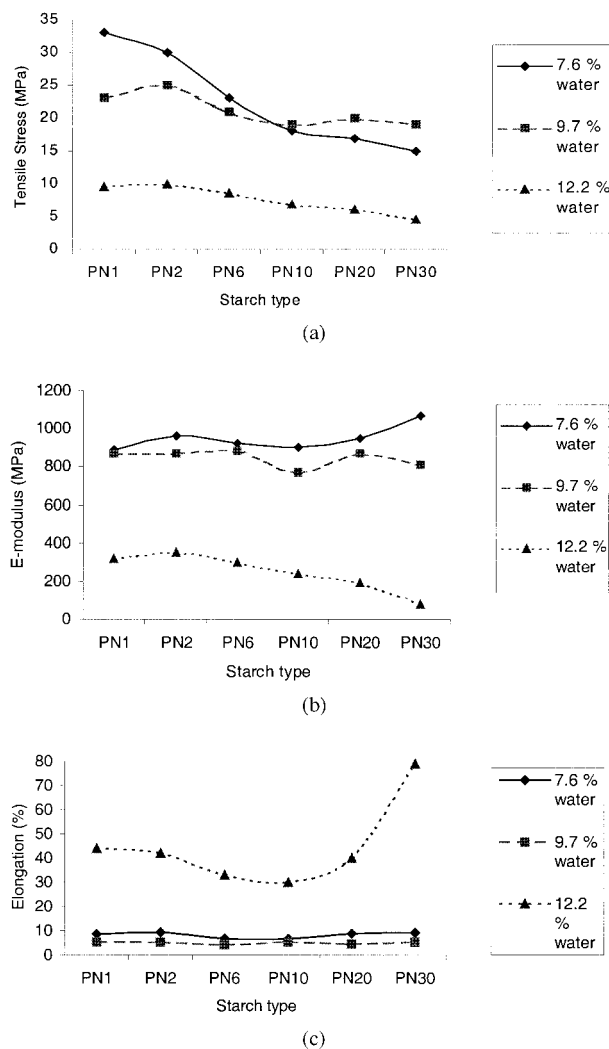

Figure 5 Influence of molding temperature on the tensile stress (a) (in the legend is the T_g shown between brackets), E-modulus (b), and elongation (c) of PN1 (▲, △) and PN30 (■, □) materials after compression molding.
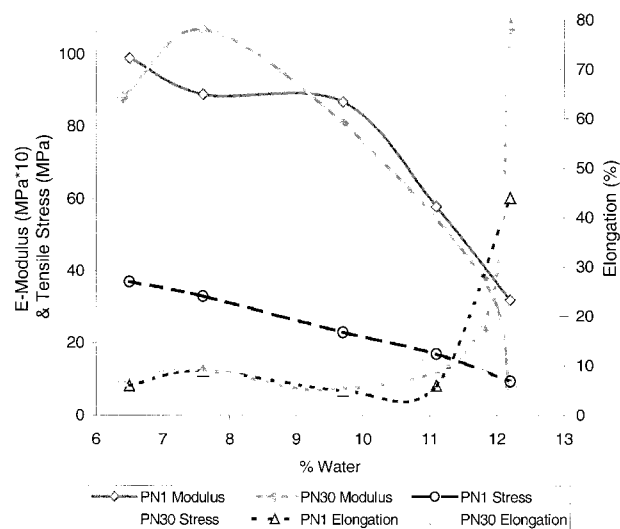
sumption. With increasing molding temperature, a more ductile behavior was observed. The stress-strain profiles showed tearing, i.e., a slower fracturing process. For the native potato starch (PN1) materials without maltodextrins, this process was only observed at molding temperatures above 180°C. For the maltodextrin materials, the changes in stress-strain behavior were more gradual and pronounced. The slower fracturing resulted in an increased elongation: 27% at 200°C and 69% at 190°C for the native starch and maltodextrin materials, respectively. Again, the tensile stress of the native starch materials had a maximum at 180°C, although the value was relatively low (17 MPa). The maximum value of the maltodextrin materials was approximately 12 MPa. A decrease in E-modulus was measured with increasing molding temperature. The effects on the maltodextrin materials were more gradual

whereas the elastic moduli were somewhat lower. The E-moduli and tensile stresses were lower compared with the molded materials stored at 30–40% RH. The lower elastic moduli, tensile strengths, and increased elongations were characteristic features of a polymeric material being plasticized through its glass-to-rubber transition.

The somewhat lower E-moduli and tensile stresses of the PN30 materials could be (partly) due to the higher water content of the PN30 materials compared with the PN1 materials (11.8 vs. 11.1%). The influence of water content on the PN1 and PN30 materials molded at 160°C is shown in Figure 7. No significant differences in the influence of water in stress-strain behavior were ob-

Figure 7 Influence of water content after storage on the mechanical properties of compression-molded ($T = 160°C$) plastic materials.

served. Remarkable is the sharp increase in elongation at approximately 11–12% water, whereas the change in tensile strength and elastic modulus is more gradual.

Influence of Maltodextrins on Stress-Strain Properties of Starch Sheets

In Table IV the structural differences and the mechanical (stress-strain) properties are shown for materials extruded with various types of maltodextrins (5% w/w on the basis of starch) added to native potato starch (95% PN1) at constant temperature, 160°C. Some typical differences are illustrated in Figure 6. After compression molding, these materials were conditioned at three humidities, 35–405, 55–65%, and 75–80% RH, respectively, and subsequently studied. The influence of water content is clearly shown. The brittle glassy materials (water contents were 7.6 and 9.7 %, respectively) showed no dependence of the elastic modulus and elongation with starch composition. The tensile strength of the glassy materials decreased slightly with increasing amount of malto-oligosaccharides. The ductile more rubber-like materials (water content is 12.2%) showed a decrease of both the tensile strength and elastic modulus with increasing amount of malto-oligosaccharides. Also the elongation was dependent on starch composition. A minimum was obtained for the PN10 material. However, some caution has to be taken with drawing conclusions from

Figure 6 Influence of maltodextrin source on mechanical properties of starch plastic materials compression molded at 160°C. Tensile stress (a), E-modulus (b), and elongation (c).

this because of the large variations in elongation (>20%).

DISCUSSION

There are several reasons that could account for the differences in structural and mechanical properties of the starch-based plastic sheets. Below, the effects of processing temperature, starch composition, and water content (after conditioning), in relation with structure and the resulting mechanical properties, will be discussed in more detail.

Effects on Morphology and Structure

Processing temperature had a pronounced effect on the degree of destructurization, plasticization, or melting of both granular starch and amorphous starch, as was also shown previously.[37,47,48] Similar effects were observed for compression-molded materials processed with different water contents.[19,20] The degree of melting/destructurization of the granular potato starch was shown in this work to be a function of the type of maltodextrin added. The addition of the maltodextrin resulted in differences in the composition of the amylose, high molecular mass starch, and saccharides. Remarkable was the fact that an increasing amount of saccharides and amorphous maltodextrin led to an increase in the amount of granular remnants and B-type residual crystallinity of the extruded granulates and at the same time less recrystallized V-type amylose. Despite the presence of an increased amount of amorphous low molecular mass starch and saccharides (which can be considered as starch plasticizers as shown by several DSC studies), the destructurization process was less effective. During compression molding, further melting of the extruded granulates, containing some granular remnants and residual B-type crystallinity, led to almost complete plasticization of the starch materials with almost no differences due to maltodextrin type. Above 130°C no residual B-type crystallinity was observed, due to the complete melting of the granular crystallinity. The differences in recrystallization, due to amylose, were clearly related to processing temperature. However, no differences could be observed due to the variations in composition of the maltodextrins. Starch molecular mass decreased due to the thermomechanical processing, both extrusion and molding. The amylose

content and amylopectin molecular mass decreased with increasing processing temperature.

In the molded starch plastics, destructurization and melting (plasticization) was performed at relatively high shear conditions and temperatures, and with limited water, the latter hindering starch granule swelling and disintegration and starch chain mobility.[38–40] An increase in processing temperature is expected to lead to an increase in starch chain mobility. Starch chain mobility determines the degree of starch plasticization and the formation of chain-chain interactions and entanglements and therewith the resulting semicrystalline network structure and the mechanical properties.[19] Furthermore, in the case of starch processed at high temperatures, in particular above 160°C, significant starch molecular breakdown occurred which would lead to a rapid change in mechanical properties.[12,21]

Influence of Water Content

With increasing water content, a decrease in elastic modulus and tensile stress was observed. This change was accompanied by an increase in elongation. At low water contents, the elastic modulus has a plateau region which is mainly determined by chain flexibility and chain-chain interactions such as H-bridging and dipolar interactions.[50,51] In amorphous polymers, chain segments are oriented at random. Even in semicrystalline polymeric materials, such as starch plastics, amorphous layers or regions exist. During preparation or processing, highly disordered structures are formed, lowering the modulus. This certainly accounts for starch-based materials in which the flexibility of the amylose chains and in particular the short outer chains of amylopectin during plasticization of the granular structures plays an important role in the height of the E-modulus plateau.

Usually the modulus drops more steeply at the glass transition region, which is characteristic of a polymer being plasticized through its glass-to-rubber transition. In the case of starch-based plastics, the changes in elongation, modulus, and tensile stress were shown to be more gradual. These broad transitions are in agreement with the broad glass transition trajectories as measured by DSC. The sharpness of the changes in stress-strain properties seemed to be dependent on plasticizer type as was shown previously.[12–14,16] The maltodextrin materials contain an increasing amount of oligosaccharides, with a chain length of

less than 20 glucose units, which have an additional plasticizing effect.[32] The T_g effects are not large because of the limited amount of malto-oligosaccharides compared with starch and the other plasticizers, water and glycerol.

Influence of Maltodextrin Type

For ductile materials (with a T_g of approximately room temperature or 19–30°C), the T_g is slightly lowered with increasing amount of malto-oligosaccharides. As expected, the E-modulus and tensile stress are lowered and the elongation is increased. The intrinsic glass transition is lower compared with starch and thus the maltodextrins act as plasticizers, lowering the T_g of the materials. This effect will increase with increasing amount of oligosaccharides in the maltodextrins.

Remarkable was the lowering of the tensile stress of the glassy-ductile materials (T_g 33–57°C) with increasing amount of malto-oligosaccharides, whereas no significant changes were observed in E-modulus for the glassy-ductile materials. With increasing amount of malto-oligosaccharides and lower molecular mass starch, the strength of the plastics is lowered. This is probably related to the broad glass transition trajectories, which results in a very gradual change in tensile stress. It seems that the tensile stress is more sensitive to slight changes in malto-oligosaccharides and molecular mass of low molecular mass starches than the E-modulus. Likely, this is due to the fact that the entanglement density is slightly lowered and therewith the strength of ductile starch plastic materials. The E-modulus reaches a plateau which is only determined by the T_g and thus by the fact that the starch chains in the glassy state are immobile. The height of the plateau is mainly determined by the rigidity of the polymer chains, and starch-starch and starch-plasticizer interactions, such as H-bonding.[50,51]

CONCLUSIONS

Variations in processing or molding temperature, in starch or maltodextrin composition and in water content were responsible for differences in morphology and crystallinity, molecular mass and glass-to-rubber transition temperature of starch-based plastic sheets. The starch-based sheets consisted of a complex semicrystalline visco-elastic polymeric material. The differences in maltodextrin compositions resulted in pronounced effects on the stress-strain behavior.

REFERENCES

1. Bastioli, C.; Lombi, R.; del Tredici, G. Italy Eur. Pat. Appl. 400,531, 1990.
2. Stepto, R. F. T.; Tomka, I.; Thoma, M. Eur. Pat. Appl. 304,401, 1989.
3. Weissner, J.; Menard, R.; Tomka, I. Eur. Pat. 537,657, 1993.
4. Sachetto, J. P.; Egli, M.; Stepto, R. F. T.; Zeller, H. Eur. Pat. Appl. 391,853, 1990.
5. Galliard, T.; Bowler, P. In: Starch: Properties and Potential; Galliard, T. Ed.; John Wiley & Sons: New York, 1987; p. 1.
6. Young, A. H. In: Starch Chemistry and Technology, 2nd Ed.; Whistler, R. L.; BeMiller, J. N.; Pascall, E. F., Eds.; Academic Press: New York, 1984; p. 249.
7. Takeda, C.; Takeda, Y.; Hizukuri, S. Carbohydr Res 1993, 246, 273.
8. Warburton, S. C.; Donald, A. M.; Smith, A. C. Carbohydr Polym 1993, 21, 17.
9. Forssell, P.; Mikkila, J.; Suortti, T.; Seppala, J.; Poutanen, K. J. Macromol Sci Pure Appl Sci 1996, A33, 703.
10. Koskinen, M.; Suortti, T.; Autio, K.; Myllarinen, P.; Poutanen, K. Ind Crops Prod 1996, 5, 23.
11. van Soest, J. J. G.; Essers, P. J Macromol Sci Pure Appl Sci 1997, A34, 1665.
12. van Soest, J. J. G.; Benes, K.; de Wit, D.; Vliegenthart, J. F. G. Polymer 1996, 37, 3543.
13. Ollett, A.-L.; Parker, R.; Smith, A. C. J Mater Sci 1991, 26, 1351.
14. Kirby, A. R.; Clark, S. A.; Parker, R.; Smith, A. C. J Mater Sci 1993, 28, 5937.
15. Shogren, R. L.; Jasberg, B. K. J Environ Polym Degrad 1994, 2, 99.
16. Shogren, R. L.; Swanson, C. L.; Thompson, A. R. Starch 1992, 44, 335.
17. van Soest, J. J. G.; de Wit, D.; Vliegenthart, J. F. G. J Appl Polym Sci 1996, 61, 1927.
18. van Soest, J. J. G.; Hulleman, S. H. D.; de Wit, D.; Vliegenthart, J. F. G. Carbohydr Polym 1996, 29, 225.
19. Hulleman, S. H. D.; Janssen, F. H. P.; Feil, H. Polymer 1998, 39, 2043.
20. van Soest, J. J. G.; Borger, D. B. J Appl Polym Sci 1997, 64, 631.

21. van Soest, J. J. G.; Benes, K.; de Wit, D. Starch 1996, 47, 429.
22. Fishman, M. L.; Coffin, D. R.; Unruh, J. J.; Ly, T. J Macromol Sci Pure Appl Sci 1996, 33, 639.
23. Albertsson, A.-C.; Karlsson, S. Acta Polym 1995, 46, 114.
24. Griffin, G. J. L. Polym Degrad Stab 1994, 45, 241.
25. Ramkumar, D.; Vaidya, U. R.; Bhattacharya, M.; Hakkarainen, M.; Albertsson, A. C.; Karlsson, S. Eur Polym J 1996, 32, 999.
26. Kotnis, M. A.; O'Brien, G. S.; Willett, J. L. J Environ Polym Degrad 1995, 3, 97.
27. Levine, H.; Slade, L. In: Industrial Polysaccharides: The Impact of Biotechnology and Advanced Methodology; Stivala, S. S.; Crescenzi, V.; Dea, I. C. M., Eds.; Gordon & Breach Science: New York, 1987; p. 387.
28. Levine, H.; Slade, L. Water Science Review; Franks, F., Ed.; University Press: Cambridge, MA, 1988; Vol. 3; p. 79.
29. Orford, P. D.; Parker, R.; Ring, S. C.; Smith, A. C. Int J Biol Macromol 1991, 11, 91.
30. Lourdin, D.; Coignard, L.; Bizot, H.; Colonna, P. Polymer 1997, 38, 4501.
31. Zeleznak, K. J.; Hoseney, R. C. Cereal Chem 1987, 64, 121.
32. Orford, P. D.; Parker, R.; Ring, S. G.; Smith, A. C. Int J Biol Macromol 1989, 11, 91.
33. Kalichevsky, M. T.; Jaroszkiewicz, E. M.; Blanshard, J. M. V. Polymer 1993, 34, 346.
34. Sworn, G.; Kasapis, S. Food Hydrocolloids 1998, 12, 283.
35. Ruan, R. R.; Zhenzhong, L.; Aijun, S.; Chen, P. L. Food Sci Technol 1998, 31, 516.
36. Gerard, J. A.; Every, D.; Sutton, K. H.; Gilpin, M. J. J Cereal Sci 1997, 26, 201.
37. Tomka, I. PCT Pat. Appl. 9,005,161, 1990.
38. Burt, D. J.; Russell, P. L. Starch 1983, 35, 354.
39. Fanon, J. E.; BeMiller, J. N. Cereal Chem 1992, 69, 456.
40. Vainionpaa, J.; Forssell, P.; Virtanen, T. Starch 1993, 45, 19.
41. van Soest, J. J. G. Agro Food Ind Hi-Tech 1997, 8, 17.
42. van Soest, J. J. G. Starch Plastics: Structure–Property Relationships. Ph.D. Dissertation, Utrecht University, P & L Press: Wageningen, 1995, p. 163.
43. van Soest, J. J. G.; Hulleman, S. H. D.; de Wit, D.; Vliegenthart, J. F. G. Ind Crops Prod 1996, 5, 11.
44. van Soest, J. J. G.; Vliegenthart, J. F. G. Trends Biotechnol 1997, 15, 208.
45. van Soest, J. J. G.; Tournois, H.; de Wit, D.; Vliegenthart, J. F. G. Carbohydr Res 1995, 279, 201.
46. della Valle, G.; Colonna, P.; Patria, A.; Vergnes, B. J Rheol 1996, 40, 347.
47. Hulleman, S. H. D.; Janssen, F. J. P.; Kalisvaart, M. G.; Feil, H. Thermoplastic Starches: Molecular Structures and Properties. Presented at the 6th Annual Meeting of the BEDPS, San Diego, CA, Sept 1997, p. 18.
48. Hulleman, S. H. D.; van Soest, J. J. G.; Feil, H. B-Type Crystallinity in Thermoplastic Starch and Its Relation with Mechanical Properties. Presented at the Starch Convention, Detmold, Germany, April 1997.
49. van Soest, J. J. G.; Hulleman, S. H. D.; de Wit, D.; Vliegenthart, J. F. G. Carbohydr Polym 1990, 29, 225.
50. Ward, I. M.; Hadley, D. W., Eds. In: An Introduction to the Mechanical Properties of Solid Polymers; Wiley & Sons: Chichester, 1993; p. 1.
51. Elias, H. C., Ed. In: An Introduction to Plastics; VCH: Weinheim, 1993; p. 1.